

# GREEN SYNTHESIS OF NANO SCALE BARIUM STANNATE CERAMIC – INFLUENCE OF CALCINATION TEMPERATURE ON PHASE PURITY AND LUMINE SCENCE PROPERTY

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## ABSTRACT

*Stannates of alkaline earth metals in the nano scale are widely explored due to their ceramic, phosphorescent, electronic properties and among them Barium stannate as a composite or single phase ceramic is significant. The present study involved two step synthesis of barium stannate using the green extract of aloe vera as the medium and at two lower calcination temperatures of 850 ° C and 1200° C.. The X-ray diffractograms indicated the phase purity of cubic perovskite structure in both the calcined samples with the average crystallite size of 52nm. The complete disappearance of barium carbonate and tin (IV) oxide phases was achieved at a temperature of 1200 ° C. The Photoluminescence study confirmed the prospect of using the sample of Barium stannate as an effective phosphor. The anti-bacterial study of the samples was not satisfactory at the given concentration and solvent. Ultimately the study provided a simple and cost effective process of preparing a multi-dimensional nano scale barium stannate ceramic.*

**KEYWORDS:** *Stannate Ceramic, Nano Composite, Aloe Vera & Barium Stannate*

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## INTRODUCTION

Nano ceramics is a compact material based on oxides, carbides, nitrides, borides and other inorganic compounds comprised of crystallites (grains) with mean size ranging up to 100nm. Advanced ceramics include inorganic and nonmetallic solid materials composed of polycrystalline sintered bodies, fine powders, single crystals, noncrystalline materials, thin or thick films, and fibres with various morphologies. Stannate based ceramics with alkaline earth metals like Calcium, Barium and Strontium are being studied for their unique luminescence properties. In this context, undoped and rare earth metals doped Barium stannates in the nano scale are investigated for their usage as multilayer capacitors, gas sensors and nanophosphors. Their unique properties are basically due to perovskite structures.

Many synthetic approaches of barium stannate ceramic powder having a sintering temperature of around 1600 °C have been attempted to suit the needs of application [1],[2],[3]. The photo and radio luminescence property of undoped and rare earth metal doped barium stannate reported by Abdul Majeed et al (2010)[4] indicated that it can act as a good host for enhanced phosphorescent property.

In this context, a simple, cost effective environment friendly method of synthesis of the nano phosphorescent barium stannate has become significant. The main objective of this synthesis is that plant extract is chosen as the acidic medium The preparation of BaSnO<sub>3</sub> was a twostep process combining the sol gel method and solid state mixing. The precursors used were BaCO<sub>3</sub>, SnCl<sub>2</sub>.H<sub>2</sub>O and a medium of plant extract which are

economically cheaper and easily available.

The method consisted of firstly, the synthesis of nano sized tin (IV) oxide from tin (II) chloride in the presence of aloe vera plant extract at a low calcination temperature of 400 °C by sol – gel process. Secondly there was solid state mixing of tin (IV) oxide obtained from the first step with barium carbonate and calcination at two relatively lower temperatures of 850 °C and 1200 °C. The samples so prepared were characterized for the size, microstructure and finally screened for photo luminescence and antibacterial activity.

## MATERIALS AND METHODS

The chemicals used for the nano scale synthesis of Barium Stannate - Tin (IV) oxide composite were tin (II) chloride dehydrate (Sigma Chemicals), *Aloe Vera* extract, barium carbonate (Sigma Chemicals), conductivity water, and ethanol.

### Experimental Procedure

The method of preparation consisted of two steps involving a sol-gel process and a solid state mixing method were carried out in the following way.

#### Step1: Preparation of Nano Tin (IV) Oxide Mediated by Aloe Vera Extract

Tin (II) chloride was mixed well with the purified fresh gel extract of *aloe Vera* plant in the ratio of 1:4, stirred vigorously for about two hours and digested overnight. The resulting gel was filtered, washed to remove impurities dried and pre-calcined in the microwave oven. It was further calcined at about 600°C for four hours and annealed. The sample tin (IV) oxide was collected and used for the following step.

#### Step2: Solid State Method

Barium carbonate powder and Tin (IV) oxide prepared in the first step were taken in the ratio 1:1. It was then subjected to solid state mixing and finely crushed. The resultant crushed powdered sample was further calcined in the muffle furnace for about 9 hrs. at a temperature of about 850°C. The same procedure was repeated with a higher calcination temperature of 1200 °C. The second calcination temperature was used to study the phase purity of the composite.

### Characterization of Barium Stannate – Tin (IV) Oxide Composite Samples

The FT-IR spectra were recorded for the samples using FT-IR (SHIMADZU) Spectrometer. The spectra were collected in the frequency range 4000-400cm<sup>-1</sup>. All spectra were recorded against the background of KBr.

The Powder X-ray Diffraction pattern of the samples was recorded using CuK $\alpha$  radiation with the diffraction angle between 10° and 70° using Rigaku MiniFlex Diffractometer.

The crystallite size, D was calculated using the Scherrer equation assuming the crystallites to be spherical. The High Resolution Scanning Microscopic (HR-SEM) images of the samples along with the relative percentage of elements (EDX) were taken using F E I QUANTA FEG 200.

The High Resolution-Transmission Electron Microscopic (HR-TEM) image and Selected Area Electron Diffraction (SAED) pattern were obtained using JEOL3010, 300KV instrument.

### Antibacterial Study by Agar Well Diffusion Method

Different concentrations of Samples (500 $\mu$ g, 1000 $\mu$ g, 1500 $\mu$ g and 2000 $\mu$ g/well) were used in this study. Nutrient Agar (NA) plates were inoculated with test organisms. The plates were evenly spread out. Then wells were prepared in the plates with a cork borer. Each well was loaded with 0.1ml of corresponding concentration of sample and 10  $\mu$ g of Tetracycline dissolved in 1 ml of DMSO was used as a Positive control for antibacterial activity. The plates were incubated for 24h at 37°C. The development of inhibition zone around the well was measured and recorded.

## RESULTS AND DISCUSSIONS

The synthesised samples of tin (IV) oxide and its composite with barium stannate calcined at 850 °C and 1200°C were dull white, pale yellow respectively and all the samples were found to be insoluble in water, ethanol and DMSO indicating the low influence of green approach on the solubility of the samples.

### Fourier Transformed Infra-Red Spectroscopy

In the case of the sample of tin (IV) oxide, there were peaks observed at 639  $\text{cm}^{-1}$ , 542  $\text{cm}^{-1}$  due to Sn-O-Sn stretching vibrations and it correlated well with the reports [4]. The broad bands in the region 3389  $\text{cm}^{-1}$  and a less intense band at 1092  $\text{cm}^{-1}$  are due to stretching vibration of –OH group. It may also be due to the physisorbed water.

The FTIR spectrum of the barium stannate composite sample calcined at 850 °C, showed an intense peak in the range of 636  $\text{cm}^{-1}$  due to Sn-O-Sn linkage. The high intense peak around 1450  $\text{cm}^{-1}$  and 856  $\text{cm}^{-1}$  are due to the stretching frequency of inorganic carbonate which correlated well with the reports of Debasish sarkar *et al.*[5]. The peak obtained in the range 3799  $\text{cm}^{-1}$  may be indicative of moisture.

The FTIR spectrum of the sample of barium stannate composite calcined at 1200 °C showed a high intense peak of 656  $\text{cm}^{-1}$  was due to the stretching frequency of Sn –O-Sn in BaSnO<sub>3</sub>. The absence of a peak in the range of 1710  $\text{cm}^{-1}$  – 1780  $\text{cm}^{-1}$  indicated the absence of carbonate. This IR result shows that as higher calcination temperature of 1200° C, there was complete removal of carbonate and existence of a single phase.

### PXRD- Powder X-Ray Diffraction Studies

The Powder X-ray Diffractogram for the samples tin (IV) oxide and nano composite barium stannate - tin (IV) oxide prepared at two different temperature are discussed as below

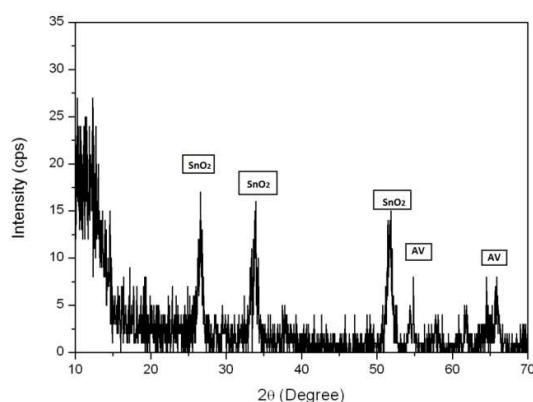


Figure 1: PXRD of Tin (IV) Oxide Prepared from Tin (II) Chloride in Aloe vera Medium

On comparing with JCPDS values (card no: 88-0287), the presence of tin (IV) oxide in the tetragonal phase was identified in the 110 and 101 plane as given in the Figure 1. The presence of less intense peaks may be due to the elemental components present in *aloe vera* which was not decomposed even at this calcinations temperature. There was complete absence of phases due to SnO indicating the complete oxidation of Sn(II) to Sn(IV). This leads to the conclusion that *aloe vera* played a vital role in the oxidation process, in the acidic medium which was contrary to the previous research reports. The average crystallite size for the SnO<sub>2</sub> calculated by Scherrer method was found to be **15 nm**.

The PXRD of the barium stannate composite prepared at the calcination temperature of 850 °C indicated the presence of cubic perovskite structure. There were also two peaks corresponding to tetragonal phase of tin (IV) oxide as per JCPDS (card no: 88-0287). The crystallite size for the most intense peak corresponding to BaSnO<sub>3</sub> was calculated by the Scherrer equation and was found to be 21 nm. The unknown peaks found in the PXRD diffract gram could be due to elemental components introduced by *Aloe vera*.

The diffract gram of the Barium stannate – tin (IV) oxide composite obtained at the calcinations temperature is given in the Figure 3. The crystallite size for the most intense peak corresponding to BaSnO<sub>3</sub> was calculated using Scherrer equation and was found to be **52 nm**. In the PXRD given above, it was found that all the intense peaks correspond to a single phase of BaSnO<sub>3</sub> and other impurity peaks were relatively less compared to the sample calcined at a lower temperature of 850°C.

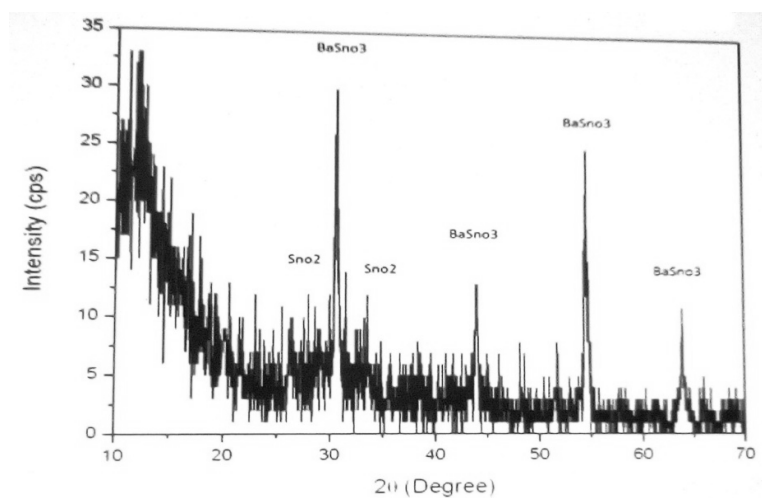


Figure 2: PXRD of Nanoscale Barium Stannate Calcined at 850°C

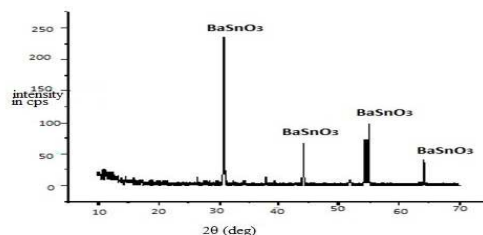
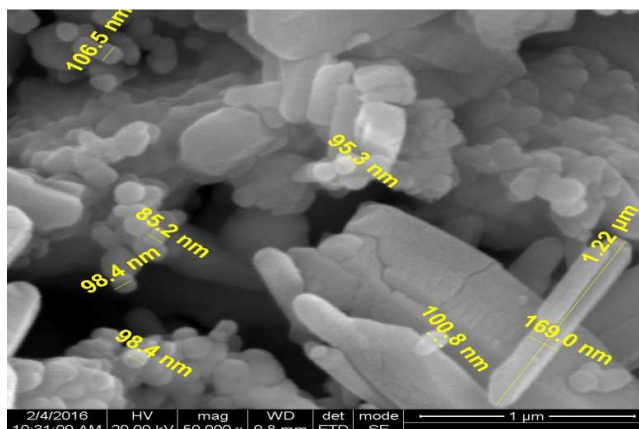


Figure 3: Pxrdo of Nanoscale Barium Stannate Calcined at 1200°C

The higher crystallite size of 52 nm may be attributed to relatively higher calcinations temperature. At higher calcinations temperature, there was better crystallinity, absence of impurity peaks due aloe vera and undissociated barium

carbonate. These results were also suggestive of the fact that the dissociation of barium carbonate was complete which was responsible for the efficient conversion of tin (IV) oxide with the barium oxide released by barium carbonate. The fact accounts for the absence of tin (IV) oxide phase in the PXRD of the sample.

#### High resolution Scanning Electron Microscopy



**Figure 4: Semimage of Nanoscale Barium Stannate Calcined at Temperature of 850 °C**

The surface morphology of the nano composite of Barium stannate and tin (IV) oxide obtained at the lower calcinations temperature of 850 °C can be identified by the SEM images given in the following Figure 4. There were agglomerations of spherical crystallites of from the SEM images, three types of morphology namely, spherical (agglomerated ) rod like and stick could be distinguished which correspond to nano sized tin (IV) oxide, Barium stannate and undissociated barium carbonate. The stick morphology of barium carbonate was also reported by Cerda *et al* ., [1]at the calcination temperature of 1200 °C and there is a rod like structure implies that it is due to the presence of barium carbonate.

#### Energy Dispersive X-Ray Analysis (EDAX)

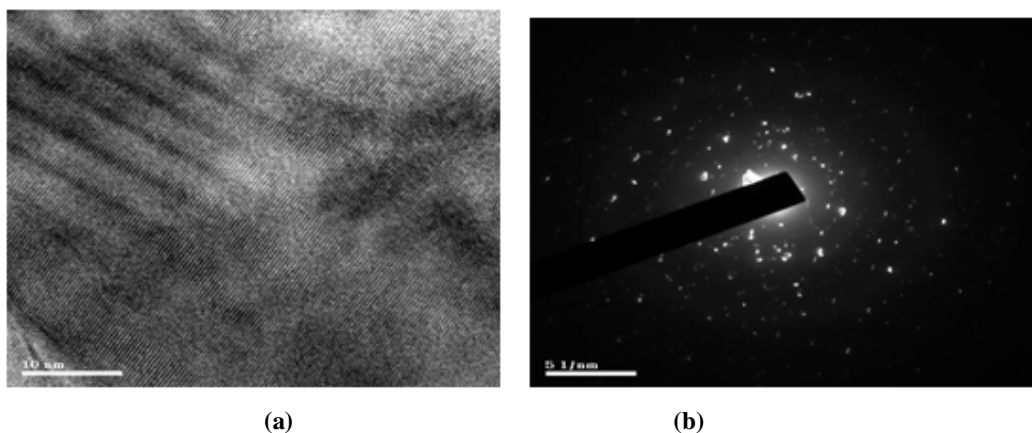
The relative percentage of elements on the surface identified by SEM image of the nano composite sample calcined at 850 °C are given by the EDAX data. The EDAX results correlated well with FTIR and PXRD results. The highest percentage of elemental Barium could be accounted by the presence Barium Stannate and the undissociated Barium Carbonate While a lesser percentage of elemental tin (compared to Barium) could be due to more of barium stannate and less of tin (IV) oxide. The presence of carbon indicated in the EDAX results could be due to carbonate species. However, the SEM and EDAX results for the barium stannate sample calcined at 1200 °C were not available.

**Table1: Relative Weight Percentage of the Nanoscale Barium Stannate Calcinedat 850°C**

Elements	Weight Percentage
Sn	32.06
Ba	41.17
O	19.02
C	07.75

### High Resolution Transmission Electron Microscopy (HR-TEM)

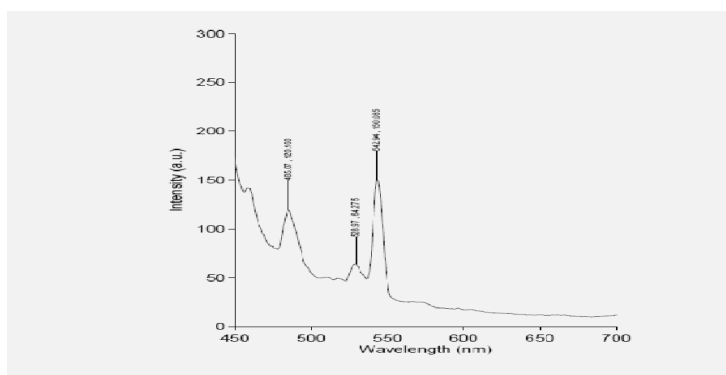
The micrographs of the nano scale Barium stannate – tin (IV) oxide are given in the Figure 5 . The TEM images of the composite sample calcined at  $850^{\circ}\text{C}$  indicated the presence of crystalline phase of Barium stannate. Also, the Selected Area Electron Diffraction (SAED) pattern gave a strong indication of the presence of two phases. This result correlated well with the results of PXRD, SEM results. The microscopic images also conformed with the crystallite size calculated by Scherrer equation.



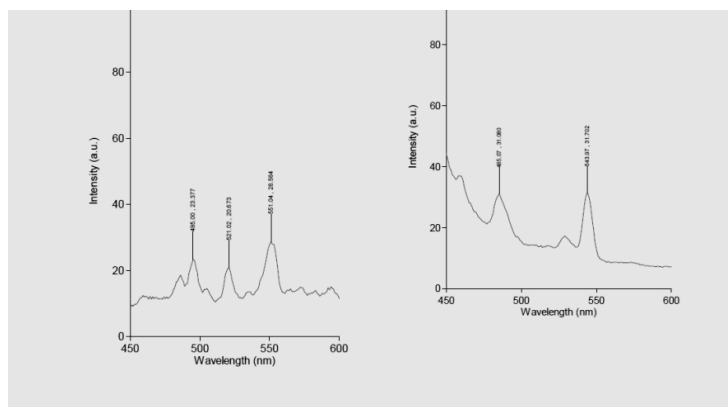
**Figure 5: TEM Images (A) and SAED Pattern (B) of the Nano Scale Barium Stannate Calcined at  $850^{\circ}\text{C}$**

### Photoluminescence Screening

There are reports available on the application of the nano scale barium stannate in terms of electrical, mechanical and photoluminescence properties. The preliminary study the photoluminescence property of the barium stannate composite calcined at two different temperatures was carried out. The emission spectra of the nano composite sample were taken and are given below in the figures 6a and 6b respectively:



**Figure 6(a): Photoluminescence Spectra of Nanoscale Barium Stannate Sample Calcined at  $850^{\circ}\text{C}$  at the Excitation wavelength of 400 nm**



**Figure 6(b): Photoluminescence Spectra of Nanoscale Barium Stannate Sample Calcined at 1200 °C at the Excitation Wavelength of 380 Nm and 400 Nm Respectively**

Photoluminescence study of the nanocomposite was carried out for the sample calcined at a temperature of 850 °C with the excitation wavelength of 400nm. Three emission bands were observed at 465 nm, 528 nm, 542 nm for the sample which was shown figure 6a. There were two broad and one sharp emission bands. The sharp intense band at 542 nm may be due to contribution from the SnO<sub>2</sub> moiety arising due to defect structure as reported by Sudhapariamala *et al* (2012) [7]. The defect structure arising due to non- stoichiometry in the composite sample play an important role in the luminescent property. The vacant sites due to oxygen contribute towards electronic traps leading to frequent electronic transition in the UV or Visible region [2].

However for the sample calcined at a higher calcinations temperature of 1200 °C, the excitation was carried out with a lower wavelength of 380nm (UV region) and a higher wavelength of 400nm as shown in the figure 6b. For the excitation at 380nm, there were three emission bands observed at 495 nm, 521 nm, and 551nm. But for excitation at 400nm there were only two emission bands at 435nm, 593nm. However, all the emission spectra are observed in visible region. The absence of tin (IV) oxide moiety in the sample was also evident.

#### Antibacterial Activity

So far there are not antibacterial activity of Barium stannate in the microscale or nanoscale. A preliminary screening study was carried out for the sample calcined at 850 °C. The bacteria taken for the testing being *Pseudomonas aeruginosa*, *Staphylococcus aureus* using agar well diffusion method.

**Table 2: Antibacterial Activity of Nano Scale Bariumstannate Calcined at 850 °C Positive control-Tetracycline; (-) No Activityzoi in mm**

Organism	Sample Concentration				
	Positive	500 µg	1000µg	1500µg	2000µg
<i>P. aeruginosa</i>	32	-	-	-	-
<i>S. aureus</i>	41	-	-	-	-

Under the given experimental condition of 500µg, 1000µg, 1500µg and 2000µg/well, there was no anti-bacterial activity for the sample calcined at 850°C. It can be concluded that the poor solubility of the sample in the solvent chosen (DMSO) for the study played a vital role. Also, it can be inferred that nano composite does not have resistance to the bacteria under given experimental condition. However further investigation with a different concentration of the sample, different solvent, and bacteria under study is required for the antimicrobial activity of the stannate sample.

## CONCLUSIONS

The two step process involving a green approach followed by two calcinations temperatures of 850 ° C and 1200 °C carried out for the synthesis of barium stannate – tin (IV) oxide composite provided an insight into effect of calcination temperatures in the phase purity of barium stannate ceramic in the nano scale. The synthesis, characterization of phase, surface morphology and the screening of the samples for photoluminescence and anti-bacterial activity strongly indicated that the method offered a simple and energy efficient approach for the nano scale phosphorescent material.

## ACKNOWLEDGEMENTS

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